

## PATENT ABSTRACTS OF JAPAN

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## (54) IRON-GROUP ALLOY ELECTROPLATING BATH

## (57)Abstract:

PURPOSE: To obtain the high-hardness iron-group alloy plating film which is smooth and has a good appearance in a wide current density range with high current efficiency.

CONSTITUTION: An iron-group alloy electroplating bath and the bath added with a reducing agent are formed from an aq. soln. contg. an iron salt, at least one kind between a nickel salt and a cobalt salt, and at least one kind of carboxylic acid selected from among a  $\geq 2$ C aliphatic carboxylic acid not contg. a hydroxyl, an aliphatic dicarboxylic acid contg. one hydroxyl or not, an aliphatic tricarboxylic acid and their salts.

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CLAIMS

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[Claim(s)]

[Claim 1] (a) or [ that the aliphatic monocarboxylic acid of iron salt, (b) nickel salt, and cobalt salt which does not contain a hydroxyl group by kind and two or more (c) carbon numbers at least, and one hydroxyl group are included ] -- or the iron-group alloy electroplating bath characterized by the bird clapper from the solution containing at least a kind of aliphatic carboxylic acids chosen from the salt of the aliphatic dicarboxylic acid which is not included, aliphatic tricarboxylic acids, and these carboxylic acids

[Claim 2] (a) or [ that the aliphatic monocarboxylic acid of iron salt, (b) nickel salt, and cobalt salt which does not contain a hydroxyl group by kind and two or more (c) carbon numbers at least and one hydroxyl group are included ] -- or the iron-group alloy electroplating bath characterized by the bird clapper from at least a kind of aliphatic carboxylic acids chosen from the salt of the aliphatic dicarboxylic acid which is not included, aliphatic tricarboxylic acids, and these carboxylic acids, and the solution containing the (d) reducing agent

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[Translation done.]

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to an iron-group alloy electroplating bath.

[0002]

[Description of the Prior Art] As for the iron-nickel-alloy plating coat, application to soft-magnetism thin films, such as surface coating of the mold for continuous casting and the magnetic head, a magnetic-shielding film, etc. is advanced now, and, as for the iron-cobalt alloy plating coat, application as a magnetic-recording film is advanced. Although a sulfuric-acid bath, chloride baths, these mixed baths, the HOUFUTSU ghost bath, etc. are industrially used as the iron-nickel-alloy plating bath for forming these plating coats, and an iron-cobalt alloy plating bath. The plating coat formed from such a plating bath is a low degree of hardness compared with the chrome plating and nickel-Lynn alloy plating for which a degree of hardness is about 300 to 500 Hv mostly, and is used as an antifriction coat, and the use range is limited. For this reason, to form more into a high degree of hardness the plating coat of an iron-group alloy which was described above is desired.

[0003]

[Means for Solving the Problem] As a result of repeating research wholeheartedly in view of the technical problem of the above-mentioned \*\*\*\* conventional technology, this invention person as a part for a metal By using the plating bath which added specific aliphatic carboxylic acids as an additive to the plating bath which contains a kind of compound of iron salt, and nickel salt and cobalt salt at least, or the plating bath which added the reducing agent further to this It finds out that the plating coat which is an iron-group alloy-plating coat of a high degree of hardness compared with the conventional thing, and moreover has smooth and good appearance is obtained with high current efficiency in the broad current density range, and came to complete this invention.

[0004] That is, this invention offers the following iron-group alloy electroplating baths.

[0005] (i) or [ that the aliphatic monocarboxylic acid of (a) iron salt, (b) nickel salt, and cobalt salt which does not contain a hydroxyl group by kind and two or more (c) carbon numbers at least, and one hydroxyl group are included ] -- or iron-group alloy electroplating bath characterized by the bird clapper from the solution containing at least a kind of aliphatic carboxylic acids chosen from the salt of the aliphatic dicarboxylic acid which is not included, aliphatic tricarboxylic acids, and these carboxylic acids

[0006] (ii) -- or [ that the aliphatic monocarboxylic acid of (a) iron salt, (b) nickel salt, and cobalt salt which does not contain a hydroxyl group by kind and two or more (c) carbon numbers at least and one hydroxyl group are included ] -- or the iron-group alloy electroplating bath characterized by the bird clapper from at least a kind of aliphatic carboxylic acids chosen from the salt of the aliphatic dicarboxylic acid which is not included, aliphatic tricarboxylic acids, and these carboxylic acids, and the solution containing the (d) reducing agent

[0007] The alloy-plating coat in which the iron-group alloy-plating bath of this invention includes two kinds, iron-nickel or iron-cobalt, or three kinds of iron-nickel-cobalt as a part for a metal when a kind is contained at least and (a) iron salt, and (b) nickel salt and cobalt salt use as a

metal salt, combining these metal salts suitably is formed.

[0008] Especially, the iron salt blended with the plating bath of this invention is not limitation-like, and if it is water-soluble, bivalent usual iron salt, it can use all. a ferrous sulfate, ferrous chloride, the first iron of a sulfamic acid, etc. can be mentioned, and independent [ in these ] as an example of such iron salt, -- or it can be used, combining suitably What is necessary is for loadings to be iron conversion and just to make them into about 1-70 g/l.

[0009] Moreover, there is especially no limitation also as nickel salt and cobalt salt, and each water-soluble nickel salt and water-soluble cobalt salt can be used. As an example of nickel salt, a nickel sulfate, a nickel chloride, nickel nitrate, nickel carbonate, a nickel acetate, a nickel amiosulfonate, methysulfonic-acid nickel, etc. can be mentioned, and a cobalt sulfate, a cobalt chloride, a cobalt nitrate, cobalt carbonate, a cobaltous acetate, sulfamic-acid cobalt, methysulfonic-acid cobalt, etc. can be mentioned as an example of cobalt salt. these metal salts are independent -- or can use it, combining suitably, and either nickel salt and cobalt salt are used, and also it can also use combining these

[0010] What is necessary is just to let a kind of compound of nickel salt and cobalt salt at least be the loadings of about 1-70 g/l by metal part conversion during a plating bath.

[0011] or [ that the aliphatic monocarboxylic acid which does not contain a hydroxyl group by two or more carbon numbers, and one hydroxyl group are included as an additive in the plating bath of this invention ] -- or it is required to blend at least a kind of aliphatic carboxylic acids chosen from the salt of the aliphatic dicarboxylic acid which is not included, aliphatic tricarboxylic acids, and these carboxylic acids By blending these aliphatic carboxylic acids, the alloy-plating coat containing carbon is formed and the plating coat obtained has a very high degree of hardness compared with the conventional iron-group alloy-plating coat. And according to the plating bath of this invention containing these aliphatic carboxylic acids, the plating coat which has smooth and good appearance with wide range current density is formed with high current efficiency.

[0012] or [ that one hydroxyl group is included by the ability mentioning an acetic acid, a propionic acid a valeric acid, butanoic acid, etc. as an example of the aliphatic monocarboxylic acid which does not contain a hydroxyl group by two or more carbon numbers ] -- or as an example of the aliphatic dicarboxylic acid which is not included, a malic acid, a malonic acid, a succinic acid, a glutaric acid, a maleic acid, a fumaric acid, etc. can be mentioned, and a citric acid etc. can be mentioned as an example of an aliphatic tricarboxylic acid Moreover, as a salt of these carboxylic acids, there is especially no limitation, if it is a water-soluble salt, it can use all, for example, it can use sodium salt, potassium salt, an ammonium salt, etc. independent [ in these aliphatic carboxylic acids ] in this invention -- or it can mix suitably and can use

[0013] It is good, and about 0.5-250 g/l, then when using these aliphatic carboxylic acids with the gestalt of an acid, as for the above-mentioned loadings of aliphatic carboxylic acids, it is desirable to consider as the loadings of about 0.5-30 g/l.

[0014] In this invention, it is required to use the above-mentioned specific aliphatic carboxylic acids as an additive, for example, it cannot replace with these aliphatic carboxylic acids, and when adding the formic acid which is an aliphatic monocarboxylic acid of a carbon number 1 or the glycolic acid which is an aliphatic monocarboxylic acid containing a hydroxyl group, a lactic acid, etc., into an electrocrystallization film, carbon hardly carries out an eutectoid and the plating coat of a high degree of hardness cannot be formed. Moreover, when adding the tartaric acid which is an aliphatic dicarboxylic acid containing two or more hydroxyl groups, it is about 1 A/dm<sup>2</sup>. It is limited to the range with the very narrow current density which produces YAKE in a deposit coat and can be used for it with neighboring current density.

[0015] In addition to the above-mentioned component, in the plating bath of this invention, a reducing agent can be added further if needed. As a reducing agent, low-grade oxides, such as reductones, such as L ascorbic acid, a gallic acid, and a hydrazine, a sodium sulfite, and a sodium nitrite, etc. can be mentioned, for example. What is necessary is for the reducing agent to be useful in order to perform continuous operation which suppressed generation of Fe<sup>3+</sup> ion and was stabilized, and just to make an addition into about 0.1-15 g/l in this invention plating bath, in order to fully demonstrate the effect by addition of a reducing agent.



[0016] In order to perform an iron-group alloy plating using the plating bath of this invention, each usual electroplating can adopt. Plating conditions are about 25–90 degrees C of bath temperature, cathode current density 0.1 – 10 A/dm<sup>2</sup>, for example, although it is not especially limitation-like. What is necessary is just to perform electroplating to the bottom of no agitating or machine churning under the conditions of a grade. Using in an acid range is appropriate for a plating bath, and it is preferably used about by pH one to six. It is desirable to use NaOH, KOH, aqueous ammonia, etc. as alkali matter as an acid using the metal salt to be used and the acid which has an anion of the same kind that what is necessary is just to perform pH adjustment of a plating bath using a suitable acid or the alkali matter according to a conventional method. In addition, when adding the above-mentioned aliphatic carboxylic acids by the plating bath of high pH region in the above-mentioned pH range, for example, about pH five to six plating bath, with the gestalt of a salt, as for the addition, it is desirable to carry out to comparatively many amounts, for example, the addition of about 50–250 g/l, within the limits of the addition mentioned above.

[0017] When each thing used for the usual iron-nickel-alloy plating, iron-cobalt alloy plating, etc. as an anode plate when the plating bath of this invention performs electroplating can be used, for example, steel is used as an anode plate, the dissolution is uniform and composition of plating liquid is mostly maintained at stability by supplying nickel salt and/or cobalt salt. Moreover, when insoluble anodes, such as carbon and platinum plating titanium, are used, continuous operation becomes possible by supplying a part for a metal, and the consumed carboxylic acid.

[0018] Although each component to blend boils comparatively the plating coat formed of the above-mentioned plating bath and it may therefore change composition in the latus range, it usually becomes the thing of 5 – 95 % of the weight of iron, nickel, and cobalt which has 95 – 5 % of the weight of kinds, and composition of about 0.2 – 3.0 % of the weight of carbon at least. It has a high degree of hardness called 600 or more Hv(s) mostly, and moreover, it is a smooth and detailed surface state, coefficient of friction is low, Vickers hardness becomes what has good abrasion resistance, and the corrosion resistance of the plating coat formed is also good.

[0019] In this invention, it is not limited especially as a plated object, but if electroplating is usually possible, all can be used.

[0020] Before performing the above-mentioned electroplating, according to a conventional method, you may perform the usual pretreatment of buffing, degreasing, being dilute-acid immersed to a plated object. it also cuts performing well-known pretreatment for various kinds of electroplating conventionally depending on the kind of plated object Moreover, after plating, you may perform operations usually performed, such as rinsing, hot water rinsing, and dryness.

[0021] The plating coat formed of this invention plating bath Are a high degree of hardness, have smooth and good appearance, and it excels in abrasion resistance, corrosion resistance, etc. if it is a thing that it can be used for various kinds of uses using the property of the above-mentioned plating coat besides the field for which the conventional iron-nickel-alloy plating coat and the iron-cobalt alloy plating coat are used and an example is given The former, quenching, carburization, nitriding, hard chromium plating, electroless plating, a chemical conversion, The machine part, electric machine instrument which were processed by thermal spraying, CVD, PVD, etc., It can use as surface treatment replaced with these processings about an implement etc. a machine tool, a work tool, a metal powder, metal mold, and a convenience -- an artisan -- also about nonmetallic products, such as a plastic, a ceramic product, textiles, paper and a wood product, and glassware After pretreating according to a conventional method, it can use as surface treatment.

[0022]

[Effect of the Invention] According to the iron-group alloy electroplating bath of this invention, compared with the conventional thing, it is the iron-group alloy-plating coat of a high degree of hardness, and it has smooth and good appearance and the plating coat excellent in abrasion resistance, corrosion resistance, etc. can be obtained with high current efficiency in the broad current density range.

[0023]

[Example] An example and the example of comparison are given to below, and the feature of this

invention is clarified further.

[0024] The plating bath (all the additions of each component are g/l) of combination of a publication was prepared to examples 1-14 and the example 1 of comparison – the 4 following table 1.

[0025]

[Table 1]

表 1

	実施例					
	1	2	3	4	5	6
硫酸第一鉄	27	27	27	27	27	27
硫酸ニッケル	11	11	11	11	11	11
硫酸コバルト						
プロピオン酸	0.5					
リンゴ酸		0.8	0.8			
コハク酸				0.7	0.7	
マレイン酸						0.7
クエン酸						
ギ酸						
L-アスコルビン酸		3.0		3.0		3.0

[0026]

[Table 2]

表 1 (続き)

	実施例					
	7	8	9	10	11	12
硫酸第一鉄	27	27	27	27	27	27
硫酸ニッケル	11	11	11			
硫酸コバルト				12	12	12
プロピオン酸				0.5		
リンゴ酸					0.8	0.8
コハク酸						
マレイン酸	0.7					
クエン酸		1.2	1.2			
ギ酸						
L-アスコルビン酸		3.0			3.0	

[0027]

[Table 3]

表 1 (続き)

	実施例		比較例			
	13	14	1	2	3	4
硫酸第一鉄	27	27	27	27	27	27
硫酸ニッケル			11	11		
硫酸コバルト	12	12			12	12
プロピオン酸						
リンゴ酸						
コハク酸						
マレイン酸						
クエン酸	1.2	1.2				
ギ酸				0.5		0.5
L-アスコルビン酸	3.0					

[0028] Using these plating baths, the copper plate was used for cathode, the griddle was used for the anode plate, and it galvanized on condition that cathode-current-density 3.0 A/dm<sup>2</sup>, the degree of bath temperature of 50 degrees C, and no stirring. The current efficiency, the nickel content, the cobalt content, the carbon content, the degree of hardness, and appearance of the obtained plating coat are shown in Table 2.

[0029]

[Table 4]

表 2

	実施例					
	1	2	3	4	5	6
電流効率 (%)	82	78	80	79	83	75
ニッケル含有率 (%)	16	16	15	17	16	18
コバルト含有率 (%)	—	—	—	—	—	—
炭素含有率 (%)	0.4	0.5	0.6	0.5	0.5	0.5
硬度 (HV)	600	680	700	690	680	680
外 観	半光沢	光沢	光沢	光沢	光沢	光沢

[0030]

[Table 5]

表 2 (続き)

	実施例					
	7	8	9	10	11	12
電流効率 (%)	80	80	85	78	82	79
ニッケル含有率 (%)	16	15	15	—	—	—
コバルト含有率 (%)	—	—	—	29	31	31
炭素含有率 (%)	0.5	0.6	0.6	0.6	0.9	0.8
硬度 (HV)	670	700	700	600	610	610
外 観	光沢	光沢	光沢	半光沢	光沢	光沢

[0031]

[Table 6]

表 2 (続き)

	実施例		比較例			
	13	14	1	2	3	4
電流効率 (%)	81	80	80	80	80	75
ニッケル含有率 (%)	—	—	12	15	—	—
コバルト含有率 (%)	32	30	—	—	22	19
炭素含有率 (%)	1.3	1.2	0.0	0.0	0.0	0.0
硬度 (HV)	630	620	450	450	400	390
外 観	光沢	光沢	半光沢	半光沢	半光沢	半光沢

[0032] The iron-group alloy-plating bath of this invention which blended the specific aliphatic carboxylic acid as an additive, and blended the reducing agent from the above result if needed further shows that the iron-group alloy-plating coat of a high degree of hardness which has good appearance is obtained with high current efficiency.

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[Translation done.]